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(54) Catalyst for purification of exhaust gas from diesel engine.

(57) A novel catalyst for use in purification of exhaust gases from diesel engines is provided. This catalyst is a flow-through type honeycomb catalyst having parallel through cells and characterized in that

(1) its cross-sectional area at the inlet part of an exhaust gas cut by a face vertical to the direction of the through cells is 10 to 100 cm², preferably 20 to 80 cm² per liter of the displacement of the engine.

(2) the hydraulic diameter of the through cells is 1.00 to 2.00 mm, preferably 1.10 to 1.40 mm, and

(3) percentage of open frontal area at the inlet part of the exhaust gas is 40 to 95 % preferably 50 to 85%. This catalyst can be one wherein a catalytically active component itself is extruded into a honeycomb shape or one wherein a catalytically active component is deposited on a honeycomb carrier.

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This invention relates to a flow-through type honeycomb catalyst for purification of harmful components in exhaust gases from diesel engines.

5 [Background Technique]

In recent years, particulate substances in diesel engine exhaust gases (composed mainly of solid carbonaceous fine particles, sulfur-containing fine particles such as sulfate particles and liquid or solid high-molecular-weight hydrocarbon fine particles) have raised an environmental and hygienic problem. These fine particles contain harmful components such as carcinogenic substances, and their particles are mostly less than 1 micron in size, and are prone to float in the air and to be inhaled upon respiration. Much consideration has therefore been given to this problem so as to set rigorous restrictions on the discharge of these fine particles from diesel engines.

As methods for purification of these fine particle substances, so-called filter methods have hitherto been carried out. That is, these filter methods are a method which comprises catching fine particle substances by filtering an exhaust gas from a diesel engine through a heat resistant gas filter (ceramic form, wire mesh, foamed metal, wall flow type ceramic honeycomb or the like), regenerating the filter by burning the accumulated carbonic fine particles using a heating means such as a burner or electric heater when pressure loss increased, and repeatedly using the regenerated filter; a method wherein frequency of the combustion and regeneration in the above method is reduced by depositing catalytic substances on the filter; a method wherein fine particle substances are burned and purified in usual exhausting conditions (gas composition and temperature), namely without particular heating by depositing catalyst substances on the filter; etc.

However, these filter methods have problems, for example, of breakage of the filter structures at combustion of the fine particle substances and regeneration of the filter; blocking of the filter by accumulation of ash components (calcium oxide, zinc oxide, phosphorus pentoxide, etc.) which are derived from the engine oil and caught together with the fine particle substances; and deterioration of activity of the catalysts. Therefore, it cannot still be declared that these filter methods are fully satisfactory methods.

On the other hand, recently according to improvements of diesel engines, there is a tendency that on the one hand content of the fine particle substances in exhaust gases from diesel engines is reduced, but on the other hand rate of SOF (components soluble in organic solvents: Soluble Organic Fraction) contained in the fine particle substances increases, and thus these exhaust gases are different from those of exhaust gases from current diesel engines in characteristics. However, there has so far been proposed no catalyst which is suitable for purification of exhaust gases having such characteristics.

35 [Object of the Invention]

Thus the object of the present invention is to provide a practical catalyst having a high purification efficiency and excellent in durability for use in purification of exhaust gases from the improved diesel engines which have a low content of fine particle substances and wherein the fine particle substances have a high content of SOF.

40 [Disclosure of the Invention]

There is provided as a catalyst capable of attaining the above object a catalyst for purification of an exhaust gas from a diesel engine which catalyst is a flow-through type honeycomb catalyst having through cells parallel to the direction of flow of the gas, wherein its cross-sectional area at the inlet of the exhaust gas cut by a face vertical to the direction of flow of the gas is 10 to 100 cm², preferably 20 to 80 cm² per liter of the displacement of the engine, the hydraulic diameter of the through cells is 1.00 to 2.00 mm, preferably 1.10 to 1.40 mm, and percentage of an open frontal area at the inlet of the exhaust gas is 40 to 95 %, preferably 50 to 85 %.

Exhaust gases to be passed through the flow-through type honeycomb catalyst of the invention are preferably those from diesel engines which contain 100 mg or less of fine particle substances per m³ of the

Generally, most of the components contained in SOF exist in a gaseous form at a temperature of 200 °C or more and exist in a form of liquid fine particles at a temperature of 200 °C or less. Thus, in case that a flow-through type honeycomb catalyst having the same shape as that of a usual catalyst for purification of exhaust gases from gasoline engines is used for purification of diesel engine exhaust gases, there arises an inconvenience that when the catalyst is exposed to temperatures of 200 °C or less, accumulation of fine particle substances due to deposition of SOF takes place at the inlet part of the flow-through type honeycomb catalyst and thereby after lapse of long time the inlet part of the cells is completely blocked. Once blockage takes place, gas amount passing through the cell decreases and performances of the catalyst is lowered, and moreover for the purpose of elimination of the blockage by the fine particle substances to regeneration of the catalyst operation conditions of the engine under high load and high revolution become necessary. However, it is difficult to appropriately obtain such high load and high revolution conditions under usual traveling, and it becomes more difficult under traffic snarls for a long time in urban district areas.

On the other hand, in case of the flow-through type honeycomb catalyst of the invention, when it is exposed to an atmosphere of diesel engine exhaust gas of 200 °C or less for a long time, blockage of the cells due to deposition of SOF does not take place, and moreover it is possible for the catalyst to display an excellent efficiency of purification of harmful components under usually employed operating conditions.

Flow-through type honeycomb catalyst of the invention must be one wherein its cross-sectional area at the inlet part of the exhaust gas cut by a face vertical to the direction of flow of the gas (i.e. the direction of the through cells) is 10 to 100 cm² per liter of the displacement of the engine. If the cross-sectional area is less than 10 cm², back pressure increases in accordance with increase of linear velocity of exhaust gas passing through each through cell, and moreover the structure is destroyed, for example, by collisions of the fine particle substances with the flow-through type honeycomb catalyst. On the other hand, if the cross-sectional area goes beyond 100 cm², SOF deposits owing to lowering of linear velocity of the exhaust gas passing through each through cell and as a result blockage of the cells increases. Further, catalysts having too large cross-sectional area are not practical because it is virtually difficult to install them in exhaust pipes of diesel engines.

Another condition of the flow-through type honeycomb catalyst of the invention is, as previously stated, that the hydraulic diameter of each cell through which an exhaust gas flows linearly must be 1.00 to 2.00 mm. In case that the hydraulic diameter is smaller than 1.00 mm, when the catalyst is exposed to an atmosphere of a diesel engine exhaust gas of 200 °C or less, blockage of the cells due to deposit of SOF at the inlet part is liable to occur. On the other hand, in case that the hydraulic diameter exceeds 2.00 mm, purification performances of the catalyst is strikingly lowered mainly due to lowering of contact efficiency of the exhaust gas with the catalyst surface inside the cells, compared to the case wherein catalyst volume and open frontal area are identical and the hydraulic diameter is 2.00 mm or less.

Still another condition of the flow-through type honeycomb catalyst of the invention is, as previously stated, that its percentage of open frontal area at the inlet part of an exhaust gas must be 40 to 95 %. If the percentage of open frontal area is less than 40 %, the geometrical surface area per unit volume the flow-through type honeycomb catalyst in contact with the exhaust gas is lowered, and thereby purification performances of the catalyst is lowered and at the same time back pressure increases. On the other hand, if the percentage of open frontal area is beyond 95 %, the separation walls constituting the flow-through type honeycomb catalyst become thin and its adequate strength cannot be obtained.

The flow-through type honeycomb catalyst of the invention may be an extruded catalyst or a deposited catalyst, but when installation thereof into diesel engine cars such as trucks is supposed, it is preferred that the catalyst is a structure having both strength and heat resistance, for example, a structure body consisting of a catalytically active component deposited on a honeycomb carrier.

With regard to the honeycomb carrier, ordinary ones can be used, and preferred examples thereby are, for example, ceramic honeycombs using as their raw materials cordierite, mullite, α -alumina, zirconia, titania, titanium phosphate, aluminum titanate, spodumene, aluminosilicate, magnesium silicate or the like; and metal honeycombs as monolithic structures using a heat resistant metal having oxidation resistance such as stainless steel or Fe-Cr-Al alloy. Particularly preferred among them are cordierite ceramic honeycomb and metal honeycombs.

Although the shape (cell shape) of the through cells of flow-through type honeycomb catalyst is not restricted, hexagon, quadrilateral, triangle and corrugation type are preferred.

Although catalytically active components in the flow-through type honeycomb catalysts of the invention are not particularly limited, preferred examples thereof are platinum, palladium, rhodium, iridium, vanadium,

substituted type having oxygen vacancy. These catalytically active components can be used alone or in combination of two or more of them. However, in case of catalysts for use in purification of exhaust gases from diesel engines using fuels having a sulfur content of 0.1 wt.% or more, it is not desirable to use platinum as the catalytically active component. The reason is that since platinum has a high oxidizing ability of sulfur dioxide (SO₂) in the exhaust gas, there is a fear that a large amount of sulfates (SO₃ and sulfuric acid mist which are oxidized products of SO₂) are produced and thereby sulfur type fine particles increase.

A flow-through type honeycomb catalyst of the invention in case of it being an extruded catalyst can be prepared by extruding catalytically active component(s) as above-described together with refractory inorganic oxide(s) such as alumina, silica, titania, zirconia or zeolite into a flow-through type honeycomb structure, for example by extrusion molding. A flow-through type honeycomb catalyst of the invention in case of it being a deposited catalyst can be prepared by depositing catalytically active component(s) as above-described directly or together with refractory inorganic oxide(s) on a honeycomb carrier as above-described.

[Industrial Applicability]

The catalyst of the present invention for use in purification of harmful components in diesel engine exhaust gases, namely a flow-through type honeycomb catalyst characterized by that its cross-sectional area at the inlet part of the exhaust gas cut by a face vertical to the direction of flow of the gas (i.e. the direction of the through holes) is 10 to 100 cm², preferably 20 to 80 cm² per liter of the displacement of the engine, the hydraulic diameter of the through cells is 1.00 to 2.00 mm, preferably 1.10 to 1.40 mm, and percentage of open frontal area at the inlet part of the exhaust gas is 40 to 95 %, preferably 50 to 85 %, does not cause blockage of the cells due to deposition of SOF even when the catalyst is exposed to an atmosphere of a diesel engine exhaust gas of 200 °C or less for a long time; and moreover makes it possible that its excellent harmful component-purifying performance is displayed with good reproducibility over a long time under usual driving conditions of diesel engines.

Further, although many of harmful components such as PAH (Poly Nuclear Aromatic hydrocarbon) which is said to be a carcinogenic substance in the fine particles are contained in SOF, the catalyst of the invention can make these substances harmless.

[Best Mode for Performing the Invention]

The present invention is further described in detail below according to examples and comparative examples, but it goes without saying that the invention is not limited to these examples.

Example 1

Alumina (3 kg) having a specific surface area of 130 m²/g was weighed and wet-pulverized together with water to give a slurry. A cylindrical flow-through type stainless steel honeycomb carrier (diameter 140 mm, length 150 mm, cell shape corrugation type, having 300 through cells per 1 in.²) was immersed in the slurry. The excess of the slurry was removed, and it was dried at 150 °C for 2 hours and calcined at 500 °C for 2 hours to obtain a structure depositing 150 g of alumina per liter of the structure.

This alumina-deposited structure was immersed in 2.5 l of a solution obtained by dissolving palladium nitrate containing 19.2 g of palladium and rhodium nitrate containing 3.8 g of rhodium in deionized water. The excess of the solution was removed, and the carrier was dried at 150 °C for 2 hours and calcined at 500 °C for 2 hours to obtain a flow-through type honeycomb catalyst deposited with 1.0 g of palladium and 0.2 g of rhodium respectively in terms of metal per liter of the structure.

This flow-through type honeycomb catalyst had an hydraulic diameter of the through cells of 1.27 mm and a percentage of open frontal area of 84 %.

Examples 2 to 16 and Comparative examples 1 to 9

Predetermined amounts of alumina were deposited on various cordierite honeycomb carriers (cell

There were indicated in Table 1 various dimensional properties of the 2000 honeycomb carriers.

5 hydraulic diameter of the through cells, percentage of open frontal area, amount of the alumina deposited and geometrical surface area in respect of the flow-through type honeycomb catalysts obtained using these carriers.

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Table 1

| | Honeycomb carrier | | | | | Honeycomb catalyst | | | |
|-----------|-------------------|------------------------------|--------------------------------|------------------------|----------------------|-------------------------|-------------------------------------|---|--|
| | Material | Shape diameter x length (mm) | Shape of the through cell | cells/ in ² | Rib thickness (mill) | Hydraulic diameter (mm) | Percentage of open frontal area (%) | Deposited Al ₂ O ₃ amount (g/l) | Geometrical surface area (m ² /l) |
| Example 1 | metal | 140 x 150 | corrugation type quadrilateral | 300 | 2 | 1.27 | 84 | 150 | 2.36 |
| " | cordierite | " | " | 400 | 6 | 1.08 | 72 | 49 | 2.68 |
| " | " | " | " | 300 | 12 | 1.10 | 57 | 51 | 2.05 |
| " | " | " | " | 300 | 8 | 1.20 | 68 | 53 | 2.23 |
| " | " | " | " | 300 | 8 | 1.11 | 56 | 160 | 2.01 |
| " | " | " | " | 200 | 12 | 1.42 | 62 | 51 | 1.76 |
| " | " | " | " | 200 | 12 | 1.35 | 58 | 106 | 1.67 |
| " | " | " | " | 200 | 12 | 1.28 | 51 | 140 | 1.59 |
| " | " | " | " | 100 | 17 | 1.91 | 57 | 102 | 1.18 |
| " | " | " | " | 100 | 17 | 1.72 | 46 | 190 | 1.11 |
| " | " | 190 x 100 | " | 400 | 6 | 1.08 | 73 | 40 | 2.80 |
| " | " | 90 x 300 | " | 400 | 6 | 1.05 | 70 | 60 | 2.41 |
| " | " | 190 x 100 | " | 200 | 12 | 1.39 | 56 | 92 | 1.71 |
| " | " | 90 x 300 | " | 200 | 12 | 1.36 | 58 | 102 | 1.65 |
| " | " | 190 x 100 | " | 100 | 17 | 1.69 | 44 | 221 | 1.03 |
| " | " | 90 x 300 | " | 100 | 17 | 1.73 | 48 | 196 | 1.11 |

(continued)

Table 1 (continued)

| | Honeycomb carrier | | | | | Honeycomb catalyst | | | |
|-------------------------------|-------------------|------------------------------------|------------------------------|--------------|-------------------------------|------------------------------------|--|---|--|
| | Material | Shape diameter x length (mm) | Shape of the through cell | cells/ in | Rib thick- ness (mm) | Hydrau- lic diameter (mm) | Percentage of open frontal area (%) | Depos- ited Al ₂ O ₃ amount (g/l) | Geo- metrical surface area (m ² /l) |
| Compar- ative example 1 | cordierite | 140 x 150 | quadrilateral | 400 | 6 | 0.96 | 60 | 148 | 2.55 |
| " 2 | " | " | " | 100 | 17 | 2.05 | 64 | 53 | 1.24 |
| " 3 | " | 230 x 50 | " | 400 | 6 | 1.02 | 73 | 57 | 2.65 |
| " 4 | " | " | " | 200 | 12 | 1.35 | 55 | 101 | 1.69 |
| " 5 | " | " | " | 100 | 17 | 1.75 | 48 | 206 | 1.09 |
| " 6 | " | 60 x 600 | " | 400 | 6 | 1.06 | 71 | 55 | 2.53 |
| " 7 | " | " | " | 200 | 12 | 1.35 | 55 | 98 | 1.60 |
| " 8 | " | " | " | 100 | 17 | 1.70 | 43 | 215 | 1.05 |
| " 9 | " | 140 x 150 | " | 100 | 17 | 1.35 | 28 | 412 | 0.83 |

Example 17

The following tests were carried out on the flow-through type honeycomb catalysts of Examples 1 to 16 and Comparative examples 1 to 9 using a commercially available turbo-charged direct injection type diesel engine (4-cylindere, 3,500 cc).

[Initial test]

Exhaust amount of fine particle substances in the exhaust gas at the inlet and outlet under the conditions of an engine revolution speed of 2,500 rpm, a torque of 10.3 kg.m and a temperature at the catalyst inlet of 300 °C was measured by the dilution tunnel method, and purification percentage (%) of the fine particle substances was determined therefrom. Further, content of gaseous hydrocarbon (THC) and content of CO in the exhaust gas at the catalyst inlet and outlet and back pressure were measured, and conversion rate (%) of THC, conversion rate (%) of CO and back pressure (mm H₂O) due to the flow-through type honeycomb catalyst were determined therefrom.

[Durability test in idling]

Durability test of the flow-through type honeycomb catalyst was carried out under the conditions of an engine revolution speed of 800 rpm, a torque of 1.0 kg.m and a catalyst inlet temperature of 80 °C, 30 hours thereafter blockage state of the catalyst at the inlet part was observed, and rate of the cells which came to be blocked (blockage percentage (%)) was determined by the following equation:

Blockage percentage (%) =

$$(1 - \frac{\text{total number of open cells after the durability test}}{\text{total number of open cells before the durability test}}) \times 100$$

The results of foregoing [Initial test] and [Durability test in idling] were indicated in Table-2 (Examples 1 to 16) and Table-3 (Comparative examples 1 to 9).

Table 2

| Catalyst | Hydraulic diameter (mm) | Percentage of open frontal area (%) | Cross-sectional area/Displacement (cm ² /l) | Idling x 30 hours Blockage percentage (%) | Fine particle substance (300 °C) Purification percentage (%) | THC (300 °C) Conversion percentage (%) | CO (300 °C) Conversion percentage (%) | Back Pressure (mmH ₂ O) |
|------------|-------------------------|-------------------------------------|--|---|--|--|---------------------------------------|------------------------------------|
| Example 1 | 1.27 | 84 | 44.0 | 0 | 55 | 74 | 82 | 101 |
| Example 2 | 1.08 | 72 | 44.0 | 4 | 49 | 69 | 78 | 295 |
| Example 3 | 1.10 | 57 | 44.0 | 0 | 51 | 74 | 84 | 216 |
| Example 4 | 1.20 | 68 | 44.0 | 0 | 56 | 68 | 74 | 159 |
| Example 5 | 1.11 | 56 | 44.0 | 0 | 52 | 67 | 78 | 226 |
| Example 6 | 1.42 | 62 | 44.0 | 0 | 47 | 62 | 73 | 124 |
| Example 7 | 1.35 | 58 | 44.0 | 0 | 53 | 71 | 75 | 153 |
| Example 8 | 1.28 | 51 | 44.0 | 0 | 57 | 76 | 83 | 214 |
| Example 9 | 1.91 | 57 | 44.0 | 0 | 39 | 49 | 61 | 97 |
| Example 10 | 1.72 | 46 | 44.0 | 0 | 45 | 52 | 62 | 141 |
| Example 11 | 1.08 | 73 | 81.0 | 6 | 50 | 65 | 71 | 67 |
| Example 12 | 1.05 | 70 | 18.2 | 0 | 48 | 62 | 73 | 905 |
| Example 13 | 1.39 | 56 | 81.0 | 0 | 47 | 64 | 69 | 69 |
| Example 14 | 1.36 | 58 | 18.2 | 0 | 48 | 64 | 70 | 818 |
| Example 15 | 1.69 | 44 | 81.0 | 0 | 41 | 46 | 54 | 55 |
| Example 16 | 1.73 | 48 | 18.2 | 0 | 43 | 51 | 58 | 679 |

Table 3

| Catalyst | Hydraulic diameter (mm) | Percentage of open frontal area (%) | Cross-sectional area/Displacement (cm ² /l) | Idling x 30 hours Blockage percentage (%) | Fine particle substance (300 °C) Purification percentage (%) | THC (300 °C) Conversion percentage (%) | CO (300 °C) Conversion percentage (%) | Back Pressure (mmHg; O) |
|-----------------------|-------------------------|-------------------------------------|--|---|--|--|---------------------------------------|-------------------------|
| Comparative example 1 | 0.96 | 60 | 44.0 | 72 | 56 | 75 | 86 | 325 |
| Comparative example 2 | 2.05 | 64 | 44.0 | 0 | 18 | 21 | 24 | 73 |
| Comparative example 3 | 1.02 | 73 | 118.7 | 57 | 41 | 59 | 63 | 23 |
| Comparative example 4 | 1.35 | 55 | 118.7 | 28 | 38 | 58 | 69 | 26 |
| Comparative example 5 | 1.75 | 48 | 118.7 | 21 | 31 | 42 | 48 | 21 |
| Comparative example 6 | 1.06 | 71 | 8.0 | 1 | 43 | 56 | 63 | 3781 |
| Comparative example 7 | 1.36 | 55 | 8.0 | 0 | 41 | 58 | 66 | 3110 |
| Comparative example 8 | 1.70 | 43 | 8.0 | 0 | 33 | 45 | 49 | 2330 |
| Comparative example 9 | 1.35 | 28 | 44.0 | 0 | 14 | 19 | 20 | 1058 |

Claims

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1. A catalyst for use in the purification of an exhaust gas from a diesel engine which catalyst is a flow-through type honeycomb catalyst having through cells parallel to the direction of flow of the gas, wherein the cross-sectional area of a face vertical to the direction of flow of exhaust at the inlet for exhaust gas is 10 to 100 cm² per liter of the displacement of the engine, the hydraulic diameter of the through cells is 1.00 to 2.00 mm, and percentage of open frontal area at the inlet for exhaust gas is 40 to 95%.

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2. A catalyst according to claim 1 wherein said cross-sectional area is 20 to 80 cm² per liter of the displacement of the engine, the hydraulic diameter is 1.10 to 1.40 mm, and the percentage of open frontal area is 50 to 85%.

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3. A catalyst according to claim 1 or 2 wherein the flow-through honeycomb catalyst is one wherein at least one catalytically active component is deposited on a metal honeycomb or ceramic honeycomb.

4. An exhaust system for a diesel engine comprising a catalyst as claimed in claim 1, 2 or 3.

5. Use of a catalyst as claimed in claim 1, 2 or 3 in the purification of an exhaust gas from a diesel engine.

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